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Overview of the Lightfastness of Commercial Printing Inks. Understanding the Mechanisms of Color Bleaching

A.J. Ragauskas and L.A. Lucia

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"Overview of the Lightfastness of Commercial Printing Inks. Understanding the Mechanisms of Color Bleaching"

by Arthur J. Ragauskas and Lucian A. Lucia
Institute of Paper Science and Technology
Atlanta, GA 30318-5794
arthur.ragauskas@ipst.gatech.edu
lucian.lucia@ipst.gatech.edu

Background

A basic understanding of the processes contributing to color bleaching (loss of color) of commercially prepared inks has been unavailable. Understanding the processes which permit fading or bleaching of inks is critical toward enhancing their lightfastness, i.e., color stability toward light exposure. About 85% of all inks have carbon black as their primary pigment, which is quite stable toward ambient lighting conditions [1]. Carbon black describes a generic class of pigments which consist of the products of the incomplete combustion of natural gas or petroleum derivatives. They are characterized by the absence of chromophores. A chromophore is a light-absorbing entity responsible for the visual perception of color [2]. The rest of the commercial pigments used for inks are colored pigments (cyans, magentas, and yellows), most of which are known to suffer minor to severe color attenuation upon prolonged, cumulative exposure to sunlight. Pigments are only one part of three key ingredients necessary to imparting the desired physical and chemical characteristics eagerly sought by commercial manufacturers. In general, inks consist of varying ratios of pigments, vehicles, and modifiers.

Components of an Ink

"Pigment" is a word derived from the Latin word *pigmentum*, which signifies paint. Indeed, pigments are naturally colored substances often derived from plant or animal sources. By necessity, they must demonstrate strong coloring power (since the applied ink film on a paper background is very thin), be hydrophobic, be inert toward heat or light drying, and display brightness. All pigments can be classified as black,

white, or colored. Black pigments currently consist of hydrocarbon particles having diameters of 100-200 nm [1, 3]. White pigments are either opaque such as the titanium or zinc oxides, or translucent such as calcium or magnesium carbonates. Colored pigments have their origin from mineral, organic, or salt precipitate substances. Pigments comprise anywhere from 5 to 25% of the total ink blend and are generally suspended in the form of an emulsion in an ink vehicle, more commonly known as a solvent [4]. They must be insoluble in the vehicle and not detract from the desired *flow* characteristics of the ink needed for a particular printing application. A list of common colored pigments with their associated lightfastness properties is displayed in Table 1 [1]. Lightfastness is measured by exposing the sample to a constant light flux from a xenon lamp to rapidly age the sample until an alteration is noted according to a gray scale. The degree of etalon tone corresponding to the alteration provides a numerical rating of the lightfastness ranging from 1 (weak) to 8 (strong).

Perhaps the most innocuous and yet most important component of an ink mixture is the ink solvent or vehicle. The main purpose of the vehicle is to transport and allow the ink to fix itself onto the printing medium. Important criteria considered in choosing a particular vehicle include the evaporation rate, viscosity, "transportation" power, and odor. For example, in *letterpress* and *litho* printing processes, the ink must display high resistance to accommodate the high pressures that can shear thin the ink [3]. Other inks may require considerably different flow characteristics which can be introduced by simply changing the particle surface properties. A vehicle must balance its ability to transport a pigment (in a solution/suspension mix) and other additives against its evaporation rate. A good vehicle will have the power to transport its guests well, but also evaporate in a manner conducive to the application of the ink. For example, *flexo/gravure* inks require fast drying, whereas *letterpress* requires a more viscous, slower drying vehicle that can actually penetrate into the paper fibers allowing the ink to dry inside the paper medium. Figure 1 depicts the relative volatility of the various commercially available vehicles [4]. A very important constituent of the vehicle is the resin. Resins are generally the heart of the vehicle since they largely determine the flow, rapidity of drying, the gloss, adhesion, flexibility, and chemical resistance of the final

product. Three general classes of resins are known: the natural consisting of rosins, asphalts, fossils, etc.; the partially synthetic or modified natural resins, such as estergum, maleic, and phenolic resins; and finally the totally synthetic resins that are comprised of polystyrenes, rubber resins, nitrocellulose, etc. By far, the partially synthetic or modified natural rosin resins are the largest classification.

Finally, the last constituents of inks are the additives or modifiers. These materials are used to improve or alter ink properties and are typically incorporated in ink manufacture. Some of the chief ingredients categorized in this class include plasticizers, waxes imparting rub resistance and slip, drying catalysts, antioxidants, surfactants for improved substrate wetting and adhesions, re-odorants, etc. One of the current specialty inks, UV curing offset inks, is based on photoinitiators and acrylates.

Evaluation of Factors Contributing to Loss of Lightfastness

A critical evaluation of the possible major causes underlying the loss of lightfastness will be given in this section. Unfortunately, a detailed and blanket mechanism elucidation of pathways contributing to loss of lightfastness is outside the scope of this article since so many active and sundry pigments are available and their environments are quite varied. Since very little research has been expended on determining the causative factors for loss of lightfastness, this article will strive to provide strong chemical basis for possible mechanisms contributing to pigment fading. Ultimately, the goals of this review are to provide a general preview of the results available for ink bleaching, suggest explanations, and spark an interest in the general scientific community to invest its resources into delving into the chemistry behind ink bleaching.

Several critical variables must be addressed in the present preview. The influence of the printing medium, the nature of the ink, the light source, and the vehicle and/or additives are the issues that have been identified as the primary factors contributing to ink bleaching. The first, and of course, most obvious variable that may play a role in ink bleaching is the printing medium that carries the ink. The print fibers act to support the

ink in strictly a physical mode. No chemical binding between ink and paper fibers has been identified. The paper is made of cellulose fibers which have a chemical crystallinity and are aligned in an ordered configuration as a result of the papermaking process. The paper fibers are therefore not expected to be reactive at ordinary temperatures and conditions. In fact, deinking technology would be severely handicapped if chemical bonding occurred between the ink and the paper. The paper allows the ink and/or vehicle to disperse on the surface or within the fibers; in the case of offset inks which are quite viscous, they dry by penetration and oxidopolymerization [1]. Inks are bound by a loose physico-mechanical interaction in or on the paper and may be exposed to air, light, or other factors to allow drying or polymerization of the ink. UV-cured inks may be dried and polymerized by the introduction of a high-energy source of light which effectively permanently binds the ink in a polymer matrix. The paper itself does not typically respond to the light treatment, remaining essentially inert.

The second and third variables which certainly affect the lightfastness of the ink are the pigment chemical characteristics and the light exposure (energy and duration of light). Although no experimental details describing the chemical mechanisms of ink bleaching are available, some possible mechanisms can be suggested based on the nature of the pigment in relation to its response to light.

Maraval and Fleidler did a quasi-chemical, though preponderantly, qualitative study on the lightfastness of inks commonly used in France [1]. Their results indicated that yellow inks tended to fade at a much more accelerated rate than magentas which likewise were somewhat less stable than cyans. Although cyan inks were quite stable over 350 hours of light aging, magenta inks faded approximately 10%, whereas yellow inks underwent anywhere from 40 % to 70 % fading. The results demonstrated that under constant lighting conditions, yellow inks underwent more profound bleaching. Unfortunately, the color trend is not applicable to all yellows. Shown in Table 1 is a list of various pigments with their corresponding lightfastness. Going from a dark color (magenta) to a lighter color (yellow) does not necessarily imply a propensity to fade. As shown, there is considerable variability in lightfastness even among the various members of the three pigment colors. For example, the *Hansa Yellows* are very stable to light.

Figure 1 shows a typical *Hansa Yellow* (**6**) molecule. As shown in the figure, it is based on a bisphenyl-azo structure. Yet, the azo backbone does not imply any added stability toward fading. Interestingly, *Persian Orange*, shown in Figure 2, which is also an azo derivative, exhibits quite poor resistance to fading in sunlight. From the above observations, knowledge of the chemical structures of the pigments, the environment of the inks, and the intensity of light, basic photochemical phenomena may be invoked to offer a fundamental understanding of the factors involved in color bleaching.

At first, it should be noted that all pigments under constant light exposure undergo bleaching. In general, the response of a pigment to sunlight is a direct function of the density of the ink. In other words, at a high optical density, the ink displays enhanced lightfastness when compared to the same ink at a lower optical density. Since the latter observation is a general phenomenon, with no ink being exempt, a rudimentary photochemically-induced (sunlight) oxidation scheme must be operating. The chemical change of any substance over time resulting in a loss of structural integrity/chemical properties can generally be attributed to oxidation, i.e., the action of oxygen on the substance causing a chemical modification of the substance. All chromophores will eventually experience oxidation at constant light levels and ambient conditions, probably due to a non-specific action on the aromatic or conjugated systems of the chromophore. For instance, anthracene will generate endoperoxides under constant sunlight exposure if an active form of oxygen, such as superoxide, is in the vicinity (see Figure 3). Superoxides can be formed by the transfer of an electron from an excited chromophore (perhaps another anthracene molecule) or by scavenging an electron from a radical or conjugated electronic system. The environment in which the pigments are suspended may also be a source of radicals, thus promoting the formation of superoxide that contributes to a general oxidation phenomenon.

Pigments are susceptible to the same nonspecific oxidation mechanisms as anthracene at long exposure levels to light and oxygen. Yet, some pigments are much more resistant than other pigments at comparable exposure times. Note that all pigments are also subject to enhanced fading at lower optical densities than at higher optical densities, suggesting that light energy can only affect a smaller proportion of the

chromophores due to less penetration of the light among the chromophores. The most stable pigments have fewer oxidizable groups (such as hydroxyls), absence of hydrolyzable linkages (such as amides), lack carbonyls on the ring, have fewer sulfonates and other charged functionalities (such as a carboxylate group or ammonium), no quinoid structures, and possess electron-stabilizing groups such as the nitro group [5].

A quinoid structure is not stable since it is a strong Lewis base, and by the abstraction of adjacent protons, the quinoid structure can easily be disrupted since it can become a hydroquinone or aromatic structure. Some unstable quinoid-like pigments include *eosin*, a yellow pigment, and *erioglaucine* (**5**), a peacock blue pigment (See Figures 1 and 2). Disruption of the quinoid-like structure in **5**, for instance, results in the formation of a triphenyl methane structure with no communication among the phenyl units, and, hence, the loss of color.

It is well known, for instance, that *indigo* which has an α, β-unsaturated ketone structure (not unlike quinones) can be protonated to yield a enol-like structure that has lost its planar conjugation and is colorless (See Figure 4). *Quercitron*, as shown in Figure 2, is a yellow lake, which has a similar unsaturated pattern as *indigo*, and rapidly fades in sunlight. The α-carbon has a hydroxyl group whose proton can be abstracted by the excited $n \rightarrow \pi^*$ state of the carbonyl, resulting in autooxidation of the hydroxyl to a carbonyl and disruption of the conjugation of the system. Such an explanation is plausible since irradiation of the same pigment by artificial light (whose energy does not correspond to the UV energy of natural sunlight) does *not* cause fading.

In fact, a carbonyl group attains an excited state having an electron-rich oxygen atom that can abstract protons, as well as a carbon-centered radical which is electrophilic and may add to oxygen or other radicals in the environment. The $n \rightarrow \pi^*$ state may be partially responsible for the specific oxidation mechanism of pigments. The instability of charged pigments may be due to their ability to engage in acid/base reactions leading to products with a different electronic character. But the latter theory does not apply in all cases, since the acid/base reactions may be offset by the presence of an electron-stabilizing group such as the nitro group. The nitro functionality may impart stability to

pigments by acting to inhibit oxidation through deactivating the ring to electrophilic reactions with oxygen or other radicals.

In addition to the electronic character of the pigments and the nature of the irradiating source, another criteria which must be considered to contribute to fading is the environment of the pigments [6]. Most pigments are suspended in a vehicle which may provide the milieu for acid/base reactions, radical reactions, or possess enough oxygen (most organic solvents have much higher concentrations of oxygen than water) for autooxidation reactions. Resins which constitute many vehicles consist of organics, some of which undergo facile oxidation reactions in the presence of oxygen. For example, abietic acid which is found in many rosins (largest resin in volume) has been shown to undergo oxidation in the presence of oxygen, as shown in Figure 5 [7-8]. It is entirely possible that a constituent of resin such as abietic acid can sensitize the oxidation of guest pigment molecules by acting as the neighboring oxidant. Vehicles that undergo oxidopolymerization in paper may also provide a viable environment for the oxidation of pigments since the oxygen-rich polymer may interact with the pigment favoring radical reactions.

In conclusion, two principal mechanisms contribute to the fading of inks. In general, a non-specific mechanism in which pigments degrade over time due to enhanced exposure to light and oxygen operates at all times, but depends on the optical density of the ink as well as the relative stability of the pigment. A more specific mechanism involved with the functionalities of the pigments and the ink environment is also posited to occur. In the latter mechanism, $n \rightarrow \pi^*$ excited states, acid/base reactions, radical adducts of oxygen, disruption of planar conjugation, and similar reactions may occur to contribute to the loss of lightfastness observed in pigments.

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Table 1.
List of several European pigments with associated lightfastness properties.[a]

MAGENTAS	Lightfastness
Red[b]	6
Univit Red Primaire[c]	5
Major Red Intense[c]	4
CYANS	
Univit Blue Primaire[b]	8
Major Blue Primaire[c]	8
YELLOWS	
Yellow[b]	7
Major Yellow Solid[c]	5
Major Yellow Primaire[b]	3

[a]Adapted from Reference 1
[b]Proprietary ink from Sun Chemical Co.
[c]Proprietary ink from Lorilleux Co.

Table 2.

List of common organic and inorganic pigments employed in inks.[a]

MAGENTAS	Lightfastness Density	
	Full Shade	Tint
Toluidine Red	excellent	good
Para Red Dark	good	poor
Barium Lithol	fair	poor
CYANS		
Monastral Blue	excellent	excellent
Peacock Blue (erioglaucine)	poor	poor
YELLOWS		
Hansa Yellow G	excellent	good
Tartrazine Yellow Lake	fair	poor

[a]Adapted from Reference 5

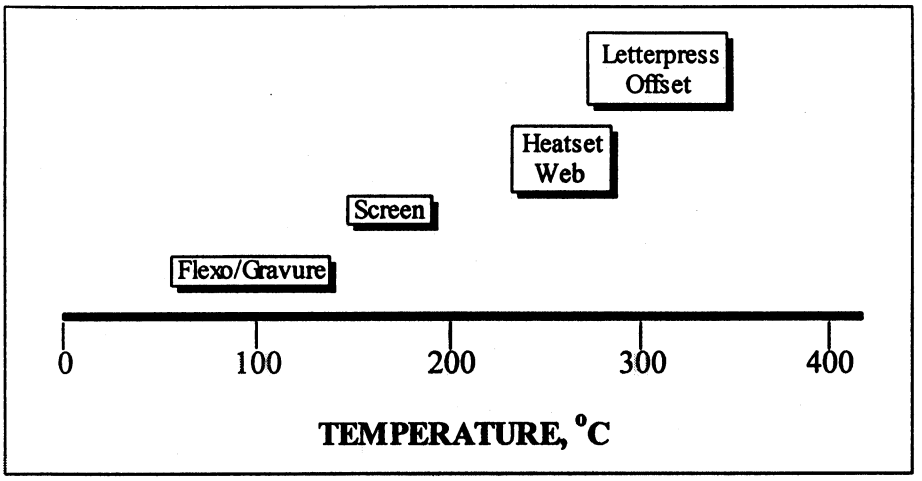

Figure 1. The range of the boiling points of the various vehicles that are used for the indicated printing processes.

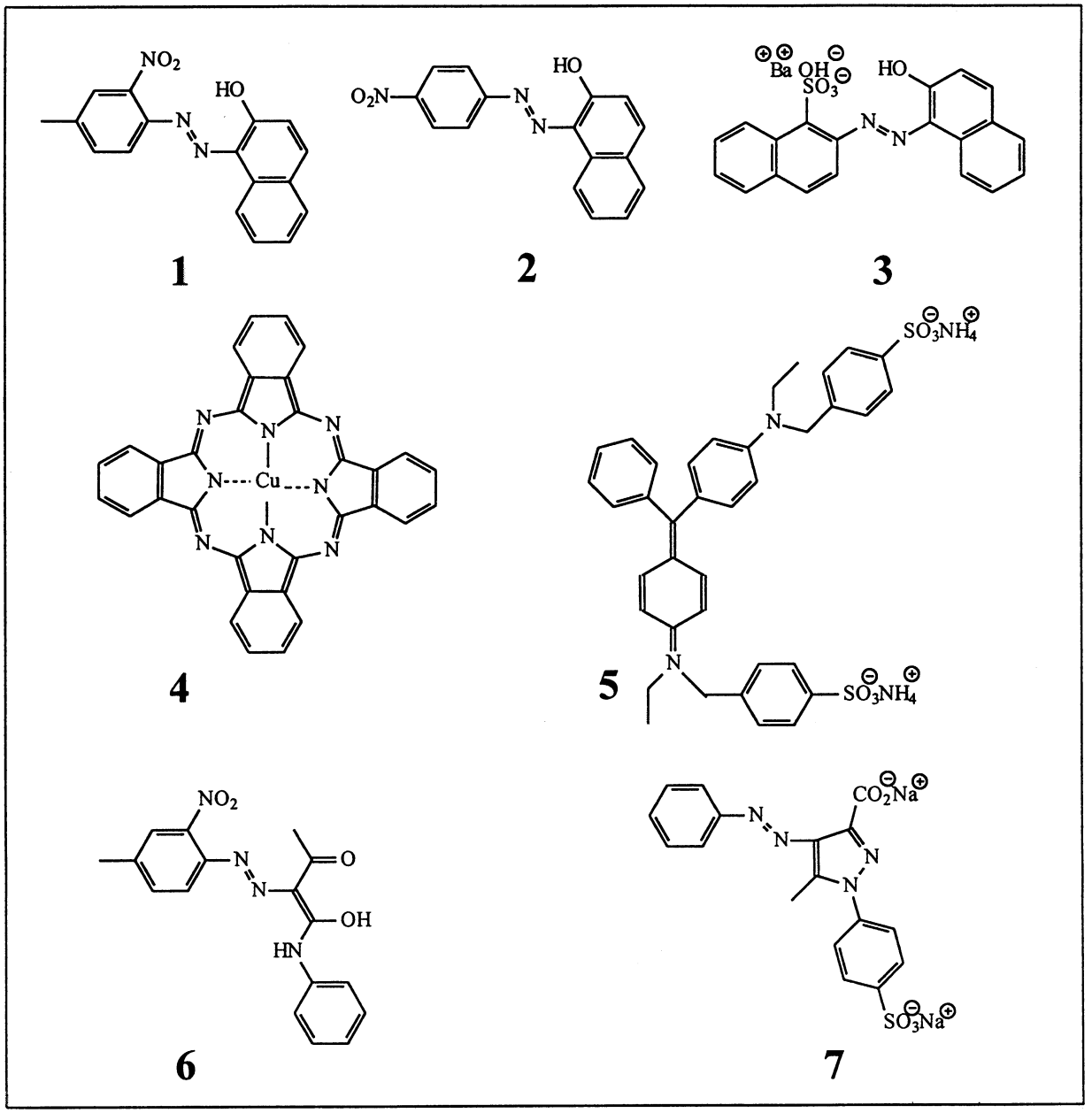

Figure 2. Shown above are the respective chemical structures of the pigments that are listed in Table 2.

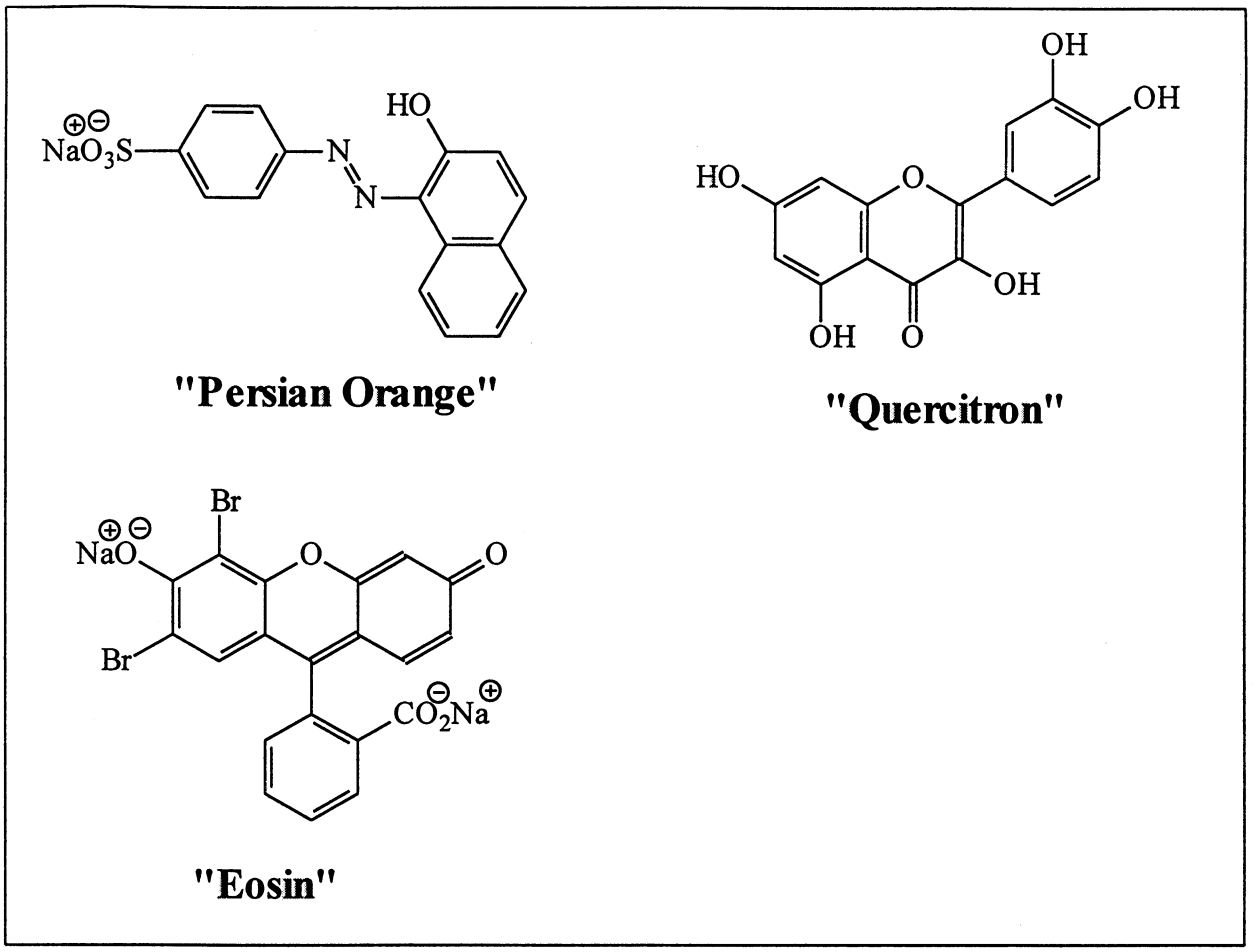

Figure 3. Other typical pigments worthy of note in this review.

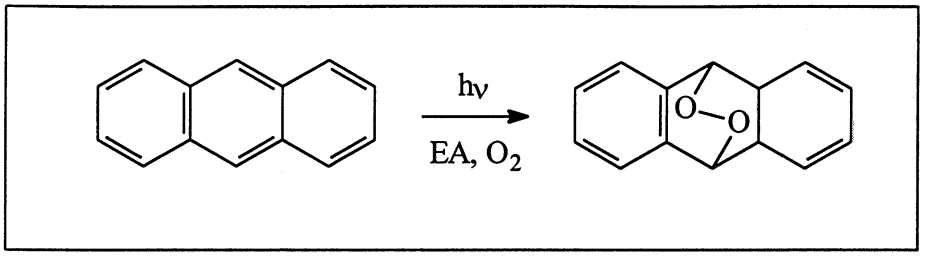

Figure 4. A generalized scheme depicting electron acceptor (EA) promoted endoperoxide formation of anthracene. The electron acceptor may stimulate electron transfer from the anthracene and later be oxidized by oxygen to yield a superoxide species. Typically, a superoxide species will add across the central ring of the arene.

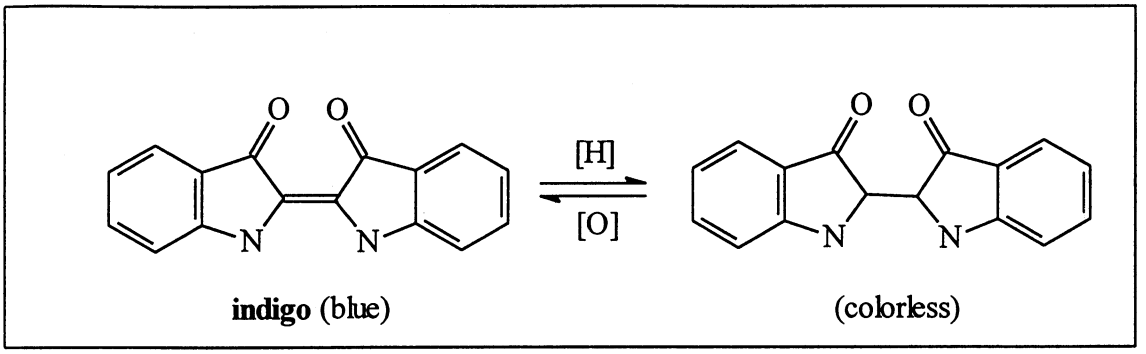

Figure 5. Indigo can undergo a reduction reaction, shown above as the forward reaction, [H], which generates a colorless form. Upon oxidation, shown above as the reverse reaction, [O], the colored form is regenerated. Protonation of the central double bond in an acidic media can lead to the colorless form.

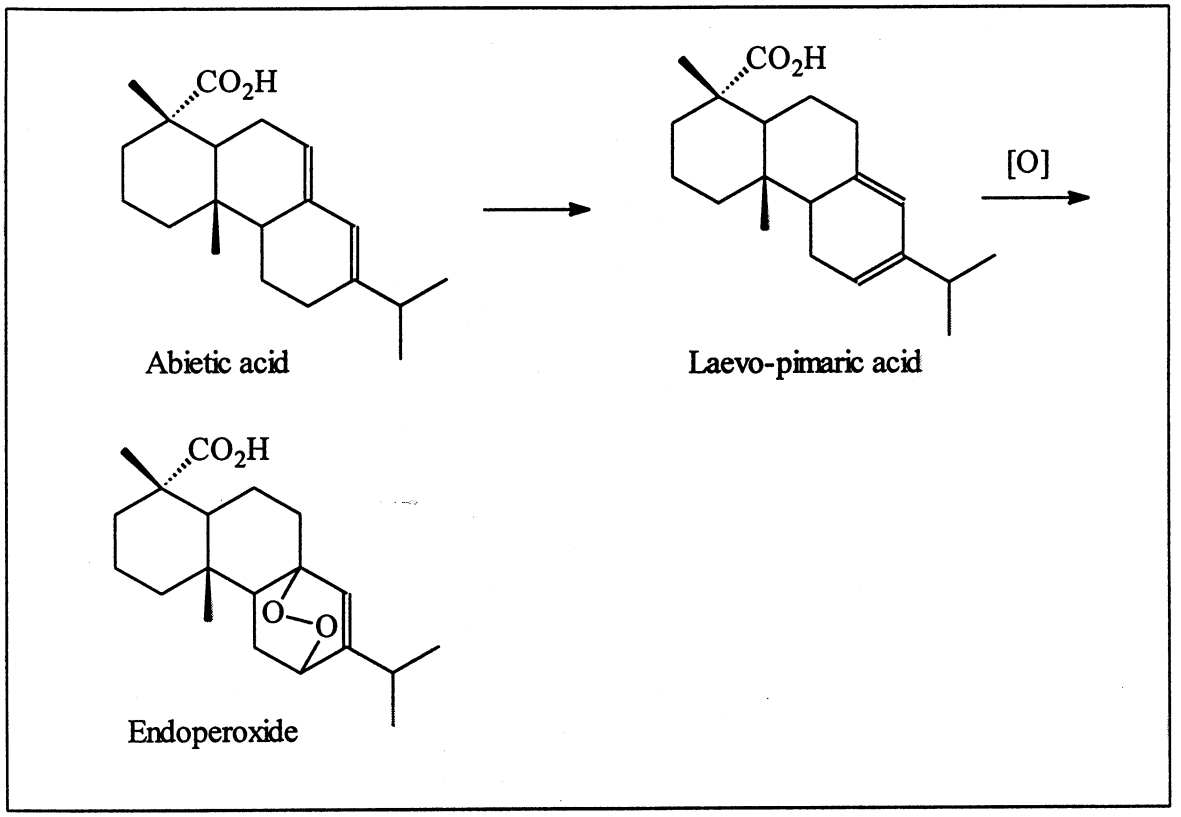

Figure 6. Shown above is one of several possible oxidation pathways available for abietic acid, one of the major constituents of rosin. Under ordinary conditions, it may form laevo-pimaric acid which is susceptible to oxidation by superoxide to yield the endoperoxide species.